PYROLYSIS OF COAL PARTICLES IN PULVERIZED FUEL FLAMES

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1. INTRODUCTION

Pyrolysis of coal converts the original material into volatile products and a solid residue. Both the formation of the volatiles and their mass transport out of the decomposing solid are usually included as parts of the pyrolysis process. The kinetics of pyrolysis, being concerned with the rate of the process, is an important consideration in dealing with pulverized coal flames since one mechanism of flame propagation depends upon the rate of appearance of combustible volatiles ahead of the flame front; and, also, heterogeneous combustion is influenced by the rate of pyrolysis behind the flame front. The need for a fundamental understanding of pulverized fuel combustion therefore places pyrolysis studies in a position of primary importance. In addition to this, further stimulation for such studies comes from other areas of current interest such as the investigation of fire spread in fundamental fire research.

This investigation was concerned with the pyrolysis of coal, and was designed to obtain information which would be directly applicable to real flames. To accomplish this end, the flame itself was chosen as the experimental system, thus eliminating potential difficulties with similitude. At the same time, the generality of the results obtained is believed to be even greater than is usually obtained in studies of coal pyrolysis.

The reason for performing this investigation is described best by considering its connection with other research in the field of pulverized fuel combustion. Considerable progress was made in this area, beginning about 1959, by performing measurements in a one-dimensional or flat flame. (7) However, in spite of the favorable capability of this technique, it had not been applied in any study of the region of the flame extending from the flame front to the point at which pyrolysis is essentially complete. Since some studies had been conducted in the regions lying on both sides of it, (1,5) this unexplored pyrolysis zone constituted a gap in the knowledge of the flame, the existence of which was both serious and surprising, in view of the assumed importance of the role of pyrolysis in the process of ignition and flame propagation. The present investigation employed a one-dimensional flame and was designed to fill this gap.

2. PREVIOUS INVESTIGATIONS

Previous investigations of the pyrolysis of coal have shown that the amount of volatile material produced by pyrolysis of a given coal depends upon the temperature to which the coal is heated and the duration of the process. In cases where the particle size is large enough to require a heating time for the center of the particle which is significantly large in comparison with the duration of the process, particle size is an important variable along with temperature and time. However, knowledge is not sufficiently advanced to permit specification of this critical size for a given time of heating.

Most investigators in this area fall into one of two broad categories depending upon their beliefs about the control of the rate of devolatilization. One group supports the proposition that the rate controlling step is the decomposition of the coal (e.g., 21,16), while the other group advocates physical control, saying that decomposition is faster than diffusion of the volatiles to the surface of the particle (e.g., 4). The investigators in each group support their views with certain experimental observations, and a unifying theory has yet to be produced.

Although the lack of agreement among previous investigators is unfortunate in many ways, the very existence of disagreement has implicit value in indicating that the cause of lack of unification might be the use of many different experimental apparatuses and conditions. Since various types of retorts and flow systems, various particle sizes, and various heating rates have been employed, the disagreement probably results from the dependence of pyrolysis rate on such factors as heating rate, particle size, and type of experimental system. Thus, the use of previous results in a system differing markedly from the original experimental conditions appears questionable, especially in the case of extreme differences.

The pulverized coal flame differs enormously from systems in which pyrolysis has been studied. Instead of a particle size of around 5 mm, the flame employs an average size of about 0.03 mm; instead of a heating time of around 30 minutes, the time in the flame is around 0.5 seconds; and, instead of a heating rate of around 1°C/sec., the rate in the flame is as high as 10^{4} °C/sec. Therefore, to extrapolate specific results from previous experiments to conditions found in the flame would be with very little confidence, so the need for suitable data in this area is obvious.

3. OBJECT

The object of this investigation was to study the pyrolysis of coal particles in pulverized coal flames, and thus to fill a gap which was found to exist in the knowledge of pulverized fuel combustion. Preliminary measurements in the flame revealed that, contrary to our expectation, a significant amount of heterogeneous combustion occurs simultaneously with rapid pyrolysis so the flame cannot be separated into two distinct zones, one containing only heterogeneous combustion and one containing only devolatilization. Therefore, in addition to pyrolysis, the study was designed to include ignition and heterogeneous combustion as well, because of the expected interdependence of these three processes.

The immediate goal of the investigation was to measure the rates of both pyrolysis and heterogeneous combustion in the flame and to employ the results thus obtained to determine: (1) important characteristics of the kinetics of pyrolysis, such as activation energy; (2) whether pyrolysis is a surface of volume reaction in the case of particle sizes in the pulverized fuel range (0-200 microns); and (3) whether the rate of pyrolysis determines the rate of ignition, and thus the rate of flame propagation.

4. EXPERIMENTAL METHOD

The experimental method consisted primarily of passing a stoichiometric cloud of pulverized bituminous coal and air down through a vertical plug flow reactor in which the particles experienced a known temperature profiel established and maintained by the combustion of the coal itself. Upon entering the reactor, the particles were heated rapidly and then pyrolyzed as they passed down through the flame. The decay of volatile matter was observed by withdrawing samples of solid material from several points appropriately spaced along the axis of propagation of the flame, and analyzing them for volatile matter, fixed carbon, and ash content. In addition to this, the temperature profile along the axis of propagation of the flame was measured. The data thus obtained consists of corresponding values of volatile content, fixed carbon content, time and temperature; this is the essential information required for studying pyrolysis kinetics.
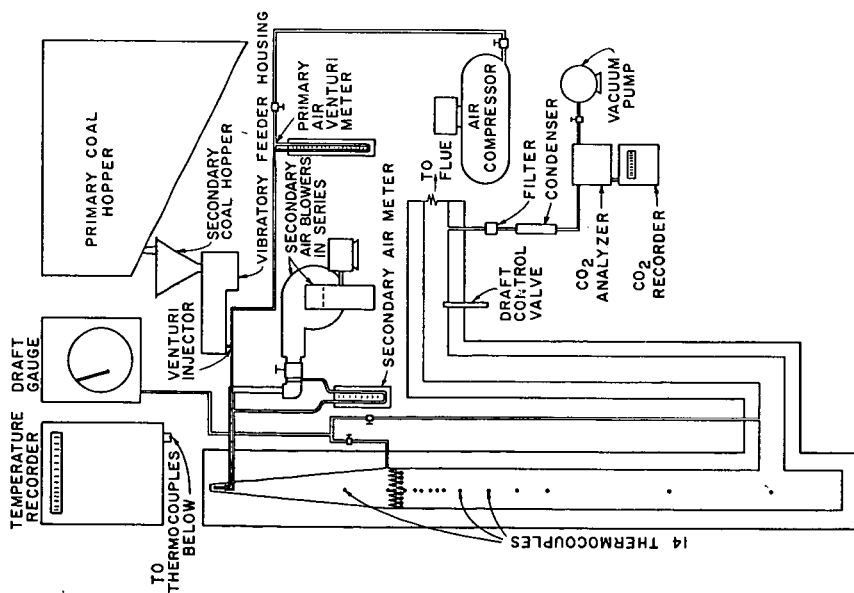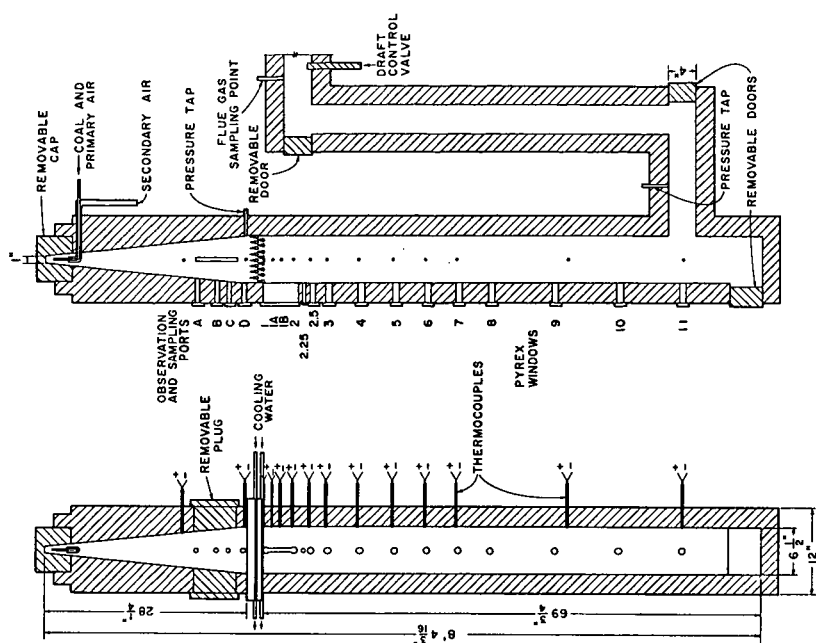
5. EQUIPMENT

5.1 Equipment for Producing and Maintaining the Flame

5.1.1 Complete Unit - The equipment for producing and maintaining the flame included the furnace, the fuel-supply system, the air-supply system and the monitoring apparatus. This is described below though further fine detail on the system can be found elsewhere. (9) Figure 1 presents schematically the complete unit.

5.1.2 Furnace - The furnace consists of a "one dimensional", pulverized fuel burner, a vertical combustion chamber, and a flue connection (see Figure 2). The flue connection provides the necessary draft for maintaining flow through the flame. The combustion chamber is of square cross section (internal dimensions of 6.5 in. x 6.5 in.), stands about 6 ft. high, and has walls composed of an insulating fire brick lining (2.5 in. thick) encased with transite sheet (0.25 in. thick).

A row of observation and sampling ports are located along the center line of the front side of the chamber at intervals determined by preliminary measurements; the region in the flame where the rate of pyrolysis and temperature increase is most rapid requires the most closely spaced sampling points. This region occurs just below the "burner".

FIGURE 2
EXPERIMENTAL FURNACE

FIGURE 1
SCHEMATIC ARRANGEMENT OF EXPERIMENTAL EQUIPMENT
FOR PRODUCING AND MAINTAINING FLAME

The "burner", which has the geometry of a truncated pyramid of square cross section, sits on top of the combustion chamber and, receiving the supply of fuel and air at its truncation, utilizes the uniform expansion of its sides to supply the cloud to the combustion chamber in plug flow. The burner expands with a total angle of 10.6° between the center lines of its sides, from a cross section of 1 in. x 1 in. at the truncation to a cross section of 6.5 in. x 6.5 in. at the base. The base of the burner is fitted with a two-row bank of water-cooled tubes staggered in such a way that radiation from the flame below cannot pass into the burner, but the cloud can pass into the chamber; the burner and the dust cloud therein are thus maintained cold. Therefore, to reach ignition temperature, the material emerging from the burner must move a finite distance into the combustion chamber and the flame is thereby forced to stabilize a finite distance below the lower surface of the tube bank. In the absence of the tubes, the flame propagates into the pyramidal section and stabilizes at a point where the flame speed is balanced by the velocity of the incoming cloud.

Since the material emerging from the burner is in plug flow, the flame stabilizes with a flat front situated perpendicular to the axis of propagation and thus assumes one-dimensionality. Recirculation currents are absent, and the history of the material collected at a given sampling point can therefore be specified with accuracy. In this respect, the furnace is similar to one constructed and used for pulverized fuel research at the University of Sheffield, (2) the principal difference being that, in the Sheffield furnace, the flame was stabilized in the diverging nozzle or cone (as described above). In our furnace, with the flat flame stabilizing in a parallel sides duct, the system is much closer to the idealized model assumed for the mathematical analysis.

5.1.3 Fuel and Air Supply System - A system was developed for supplying fuel and air at adequately constant and controllable rates and mixture ratios (see Figures 1 and 3). A metered stream of compressed air (primary air) collects the coal from a small funnel fitted into the throat of an asymmetric venturi and injects it up against the truncation of the burner where mixing occurs with a second stream of metered air (secondary air). Utilizing two separate air supplies permits independent control of the supplies of fuel and air, and impinging both streams against the truncation of the burner creates enough turbulence to ensure dispersion of the dust in the resulting cloud.

The rate of coal feed is controlled by adjusting the intensity of vibration of a vibratory feeder enclosed with the venturi funnel in an air-tight box. The coal drops into the venturi funnel after traveling on the feeder tray from a small hopper designed to serve as a self-regulating valve between a larger primary hopper and the rest of the feed system. Continuous circulation of the bed in the primary hopper prevents packing. With this system, the average variation in the rate of coal feed during an experimental run was measured to be 2.8%, and the variation in the air supply rate was nill.

5.1.4 Monitoring Apparatus - Operation under steady conditions was ensured by monitoring the flame with three independent measuring and recording instruments (see Figures 1 and 2): (a) the temperature along the inside surface of one wall was sensed by fourteen sheathed Pt/Pt 10% Rh thermocouples appropriately spaced along the length of the flame, and continuously plotted by a 24-point potentiometer/recorder; (b) the content of carbon dioxide in the combustion gases was monitored by analyzing a continuous sample of flue gas with a thermal conductivity instrument; and (c) the pressure at each end of the combustion chamber was monitored by an oil type, inverted-bell draft gauge. Of the three, the first was by far the most useful; a significant change in the flame was reflected in the wall-temperature profile in a matter of seconds, and could then be corrected.

5.2 Equipment for Probing the Flame

5.2.1 Solid-Sampling Probe - A water-cooled suction instrument was built which collects a sample of particles representatave of the material at a point in the flame and quenches it at a sufficiently rapid rate (see Figure 4). The probe is composed of three individually cooled units and is easily disassembled to facilitate cleaning. The requirement that the sampling operation exert no significant influence on the flame forced us to minimize the diameter of the part of the probe penetrating the flame; this resulted in the filter chamber being located outside the flame. In the zone of the flame where particles become sticky because of primary decomposition, clogging of the sampling tube is a menace which prevented us from using a smaller diameter probe.

When the probe is in sampling position, the nozzle points vertically upward and, given the proper suction velocity, collects particles without changing their flow direction until they are already inside the probe. A rotameter and valve in the suction line allowed the proper suction velocity /about five times the main stream velocity(11)/ to be obtained.

A substantial amount of the sample does not reach the filter chamber but instead collects on the cold walls of the probe. We were therefore careful to save the whole sample to avoid both selectivity and contamination.

5.2.2 Suction Pyrometer - A single-shield suction pyrometer was built for temperature measurement (see Figure 5). The instrument uses a Pt/Pt 10% Rh thermocouple, and its
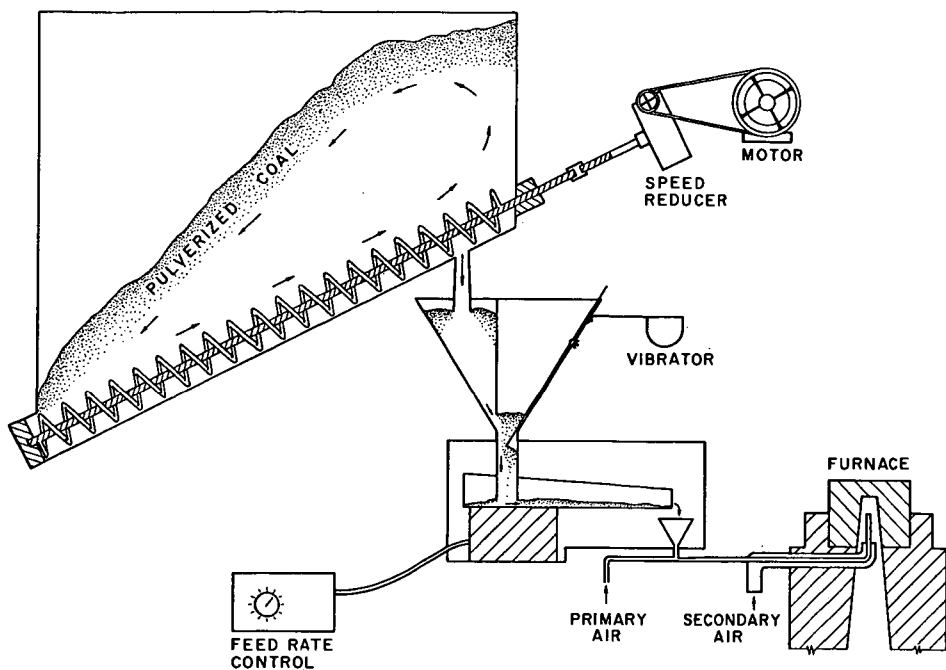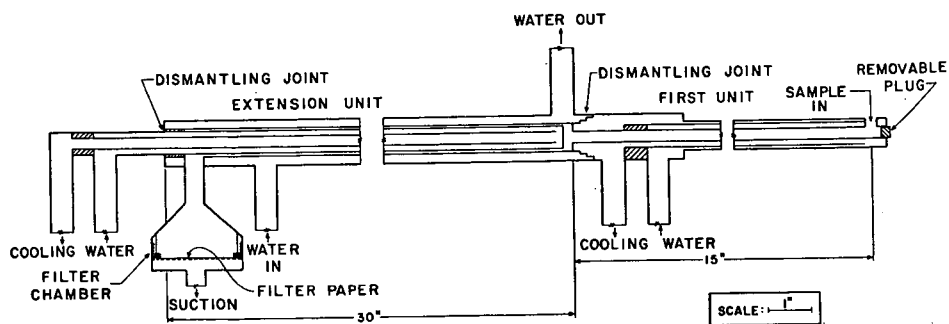
FIGURE 3
FUEL SUPPLY SYSTEM

FIGURE 4
SOLID-SAMPLING PROBE

radiation shield and thermocouple protection sheath are made of either mullite or high temperature alumina. The pyrometer is composed of two individually cooled units and a filter chamber, and is easily disassembled for cleaning.

This type of instrument measures a temperature which lies somewhere between that of the particles and that of the gas. (12) However, according to our calculations, there is no significant difference between those two temperatures for particle sizes below about 200 microns, even in the region of the flame where the rate of heating is most rapid. Therefore, the temperature of the particles can be taken as the suction pyrometer temperature.

5.2.3 Probe Supporter and Positioner - Apparatus used for supporting the sampling probe and pyrometer consists of a frame which slides vertically in a track along the front of the furnace (see Figure 6). The track is graduated to permit precision in positioning the instruments: a given sampling point is located with an error of less than 0.5 mm in all three directions.

5.3 Equipment for Analyzing Samples

The equipment used for analyzing the solid samples obtained from the flame was basically the standard apparatus specified by the A.S.T.M. for the proximate analysis of coal. However, the A.S.T.M. directions are based on the availability of plenty of coal (2 gram samples) whereas, in this investigation, the collection of such a large quantity was impossible. The collection also was both time consuming and tedious, so the A.S.T.M. specifications were modified to suit the condition of a limited supply of material for each sample (down to 50 mg). Three alterations were introduced; (1) smaller containers were used for the samples in each test in order to attain the desired accuracy of weighing (Coors size 000 with size B lid); (2) the residue from the volatile matter test was used in the ash test in order to eliminate the need for two different samples; and (3) a small stream of dry nitrogen was passed through the volatile matter furnace to prevent combustion of samples which, either because of previous devolatilization or small size, produced insufficient volatiles to displace the surrounding air. The necessity for these alterations, and the desired effectiveness of each, were demonstrated by extensive preliminary testing. (9)

6. EXPERIMENTAL MEASUREMENTS

6.1 Preliminary Tests

Two important aspects of the experimental system were tested prior to performing the main measurements. These were (1) the absence of recirculation currents in the flame and (2) the quenching ability of the solid sampling probe. A description of each test is given below.

(i) Even before the tests were conducted the flame was believed to be adequately one-dimensional (and therefore free of recirculation currents) on the grounds that: (a) with regard to one-dimensionality, this system is very similar to one at the University of Sheffield which was shown experimentally (3) to produce a one-dimensional flame; and (b) the visually observed flame front was flat. Nevertheless, since our ability to specify the history of a given sample of solid material depends on the absence of recirculation currents, additional verification of this feature was essential. To attain this, the following tracer experiment was conducted. A stream of helium amounting to 7 per cent by volume of the total flow in the furnace was injected into the flame through a 1/4 inch ceramic tube positioned successively at various points along the axis of propagation of the flame and along the center lines of the inside surfaces of two adjacent walls. During injection at each point, a water-cooled probe was used to withdraw samples of flame gases at points displaced both horizontally and vertically from the seeding point. The samples collected were analyzed for helium content with a gas chromatograph capable of detecting traces of helium amounting to less than 0.01 per cent by volume.

The flame and the preignition region between the burner and the flame front were surveyed with this technique: at no point was helium found to be carried vertically upwards as would be expected if a recirculation current were present. Instead, the seeding stream always flowed downwards, spreading laterally at the slow rate expected from molecular diffusion. The conclusion was, therefore, that the flame is free of recirculation currents.

(ii) The quenching ability of the solid sampling probe was determined by measuring the temperature profile in the stream of sampled material flowing through the probe. This was accomplished with a narrow-shield suction pyrometer extending into the probe and positioned successively at several points from the inlet to the exit. As was expected, we found that the temperature of the material at a given position in the probe increases with both increasing suction velocity and increasing flame temperature. When sampling from the hottest point in the flame with the suction velocity employed in the actual experimental runs, the first unit of the probe (see Figure 4) was found to cool the sample from 1520°C (the flame temperature) down to 420°C in a period of 0.01 seconds, and the second, larger unit cooled the sample on down to about 25°C in
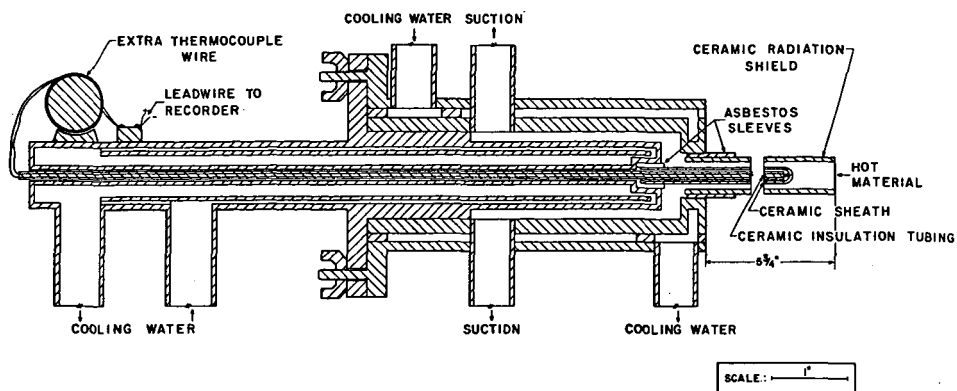
FIGURE 5
SUCTION PYROMETER

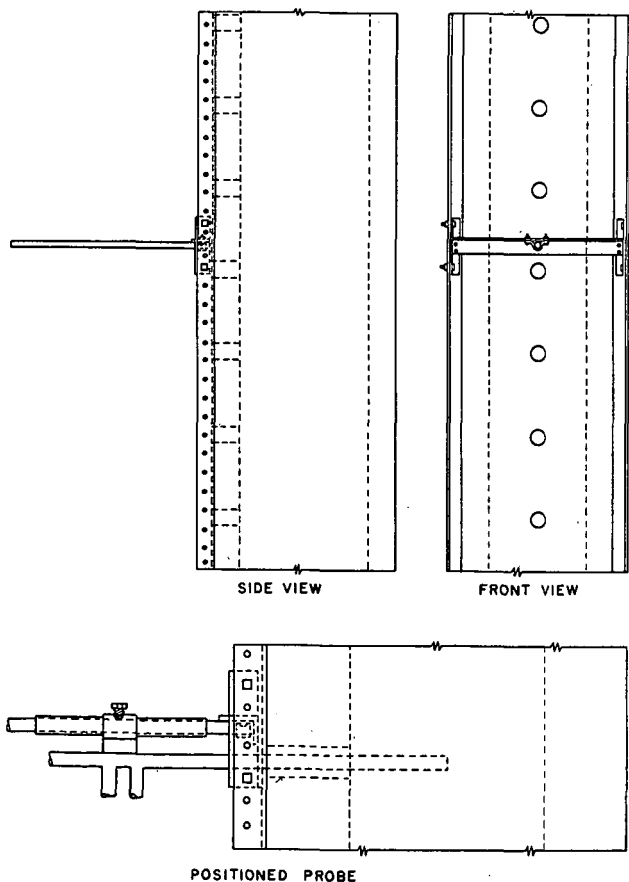
SIDE VIEW   FRONT VIEW

POSITIONED PROBE

FIGURE 6
PROBE SUPPORTER AND POSITIONER

less than 0.1 seconds. The solid particles leaving the first unit of the probe can be regarded as quenched since the rate of pyrolysis is extremely slow at 420°C, and the time required to attain this inactive state is suitably small. Therefore, the quenching ability of the probe is acceptable.

6.2 Measurements in the Flame

6.2.1 Scope of the Measurements – A single set of experimental conditions was employed during the whole investigation and no attempt was made to study the effect produced on pyrolysis by varying a certain input quantity (feet rate or fuel/air ratio). Runs were repeated only for the purpose of increasing confidence in the observations.

In each experimental run, solid samples were taken and flame temperatures were measured along the flame axis by utilizing the ports in the furnace wall (see Figure 2). In addition to some preliminary exploratory runs, seven data producing runs, each lasting about sixteen hours, were conducted. The samples obtained were analyzed for ash, volatile matter, and fixed carbon.

6.2.2 Experimental Coal – The coal used (trade name, Grade E-5 Ground Coal) was purchased in the pulverized form from the Penn-Rilton Company. The coal came from the Mathies Mine where it is taken from the Pittsburgh seam and ground in a Raymond-Hammer-Screen Mill. The particle size distribution (see Figure 7) was measured with a Coulter Counter; some variation in the size of the coal used in the different runs was found, but this was small enough to be acceptable. The proximate analysis of the coal is as follows: Ash - 3.86% of dry coal; Moisture – 0.97% of raw coal; Volatile Matter - 37.35% of dry, ash-free coal; and Fixed Carbon - 62.65% of dry, ash-free coal.

6.2.3 Experimental Conditions – The flame studied in each run was produced under the following set of conditions:

(i)	Coal feed rate	10 pounds per hour
(ii)	Flow rate of primary air	6.9 SCFM (1 atm and 70°F)
(iii)	Flow rate of secondary air	11.4 SCFM
(iv)	Fuel-air ratio	0.135 grams/liter or oz/cu.ft.(at 1 atm and 0°C)

The procedure for stabilizing the flame included first preheating the furnace with a natural gas flame and then making a transition from gas to coal. When the change to coal was completed, a sufficient lapse of time was allowed to ensure stabilized flame conditions. The three monitoring devices described earlier were used to determine flame stability.

6.2.4 Experimental Procedure – The collection of solid samples and measurement of flame temperature followed a procedure in which the probe positioner was fixed at a given port and both instruments were used there before proceeding on to the next port. After collecting a sample of solid material (which required a suction time of about three minutes), the probe and filter chamber were disassembled, the sample was removed and the inside of the probe was thoroughly cleaned. The samples were placed in the same covered crucibles in which they were subsequently analyzed, and then stored in a desiccator.

In the temperature measurements, the thermocouple protection sheaths were replaced after two or three measurements because a coating of ash deposits soon became thick enough to affect the readings. Also, the instrument was disassembled and cleaned before the accumulation of solid material became large enough to affect seriously the flow past the thermocouple.

In each experimental run, three and sometimes four individual samples were collected at each sampled port, and at least 10 and sometimes up to 14 ports were sampled.

6.3 Analysis of Samples

The crucibles containing the samples from the probe were first placed in the moisture oven (with their lids off) for drying. The initial weight was not measured since the moisture content of the samples was not needed, though drying was required since any moisture left in the samples would appear later as apparent volatile material. After moisture removal, the covered samples were cooled in a desiccator, weighed, devolatilized in the volatile furnace (7 minutes at 950°C), cooled in the desiccator, and weighed for volatile loss, all without removing the lids.

Next, the samples, i.e., the remains from the volatile tests, were placed in the ash furnace with the lids removed from the crucibles. After complete burning of the samples, the lids were replaced on the crucibles and the samples were once again cooled in a desiccator. After cooling, the covered crucibles were weighed both with and without the ash remains of the samples.

These four weighings allowed calculation of the contents of volatile matter and ash, both expressed as a percentage of the original, dry sample. The percentage of fixed carbon was then determined by subtracting the sum of these two percentages from 100.
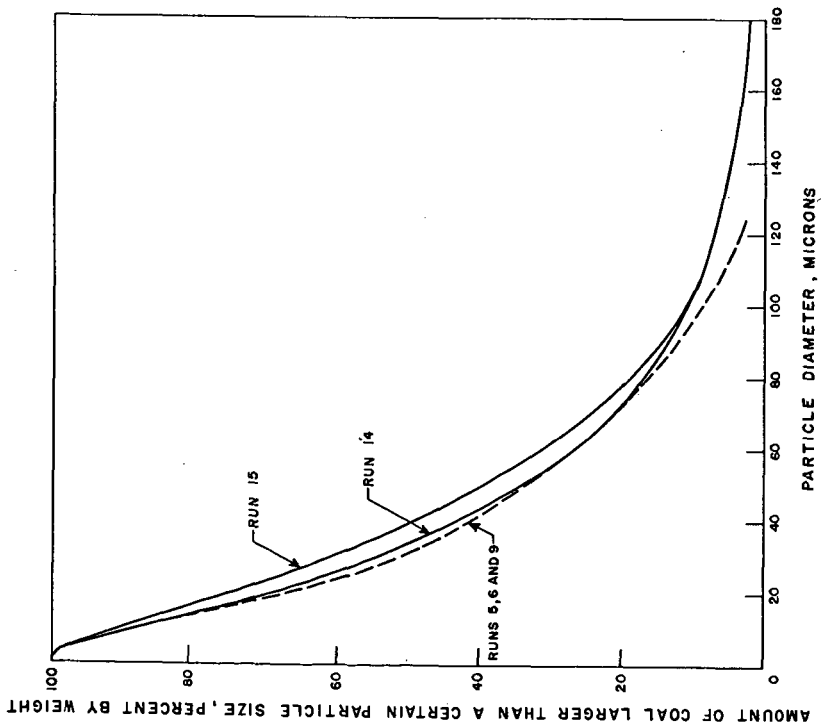
FIGURE 8
VOLATILE MATTER CONTENT OF SOLID MATERIAL DURING
PASSAGE THROUGH FLAME

FIGURE 7
SIZE DISTRIBUTION OF COAL USED IN EXPERIMENTAL RUNS

7. RESULTS

In the following presentation, the data from a single experimental run are used for illustration and can be accepted as a representative example of the data collected in all the runs. Presentation of the data from the other six runs adds no extra value other than illustrating the agreement between runs; this has already been done and the data found to be adequately reproducible. (9)

7.1 Basic Data

The composition of solid material and the temperature of the flame, both measured along the axis of propagation, constitute the basic data obtained (see Figures 8-11). Unexpected observations are that the particles attain a temperature of around 1100°C before either ignition or rapid pyrolysis occurs, and that a significant amount of volatile material exists in the unburned residue leaving the flame. This volatile residue persists over a substantial length of the flame and therefore appears to be a relatively stable component of the original volatile matter. Another significant point to observe is that rapid pyrolysis does not begin until after ignition.

The temperature of the particles begins to rise as they pass through the bank of water-cooled tubes (see Figure 11). Radiation from the flame front first becomes visible to the particles when they are inside the bank; upon emerging from it, their temperature is up to about 480°C. Nevertheless, the composition of the particles remains unchanged until they leave the lower surface of the tubes.

7.2 Useful Arrangement of Data

Since the percentages of volatile material and fixed carbon on a total weight basis are interdependent, a more meaningful arrangement of the data was attained by calculating the two compositions on the basis of their initial values. This allows the contribution to devolatilization of both gaseous evolution and heterogeneous combustion to be studied independently. Also, time is more useful than distance as a kinetics parameter. Accordingly, the basic data can be arranged more usefully as described below.

The conversion from distance to time was made using the known value of the cold flow rate through the combustion chamber and the measured temperature profile. In this calculation it was assumed that the volume change resulting from chemical reaction is small enough to be neglected, an assumption which can be shown to be permissible.

The fractions of the original volatile matter and fixed carbon remaining in the particles at each sampling point were calculated using the ash as a tracer. To achieve this, the following equations, which result from a simple derivation, were employed:

$$\left[(V.M.)/(V.M.)_o \right] = \left[(\%V.M.)/(\% Ash) \right] \left[(\% Ash)_o/(\%V.M.)_o \right] \tag{1}$$

$$\left[(F.C.)/(F.C.)_o \right] = \left[(\%F.C.)/(\% Ash) \right] \left[(\% Ash)_o/(\%F.C.)_o \right] \tag{2}$$

V.M. and F.C. are the weights of volatile matter and fixed carbon remaining in the solid material; $\%F.C.$, $\%V.M.$ and $\%$ Ash are the percentages of the dry material represented by fixed carbon, volatile material and ash; and, the subscript o refers to the original coal. The results of these manipulations of the data are presented in Figures 12 and 13.

The magnitude of the ratio V.M./F.C. at a given point in the flame is indicative of the rate of volatile loss by gaseous evolution relative to the rate of loss by heterogeneous combustion at that particular point. The decay of this ratio with degree of burnout, represented by $(F.C.)/F.C._o$, is shown in Figure 14.

8. ANALYSIS AND INTERPRETATION

8.1 Qualitative Analysis

8.1.1 Basic Qualitative Behavior

- The data presented above furnish a general picture of pyrolysis in the flame. Slow pyrolysis begins when the particles enter the hot combustion chamber at the lower surface of the water-cooled tube bank, and continues for a short time with no accompanying loss of fixed carbon (see Figures 12 and 13). After a period of about 0.05 seconds, heterogeneous combustion, and hence the loss of fixed carbon, begins abruptly with a very rapid rate at a point corresponding to the location of the visually observed flame front (see Figure 13). Soon after ignition, the rate of volatile loss becomes very rapid since volatile matter, in addition to being lost by pure evolution into the gaseous state, is also burned in the
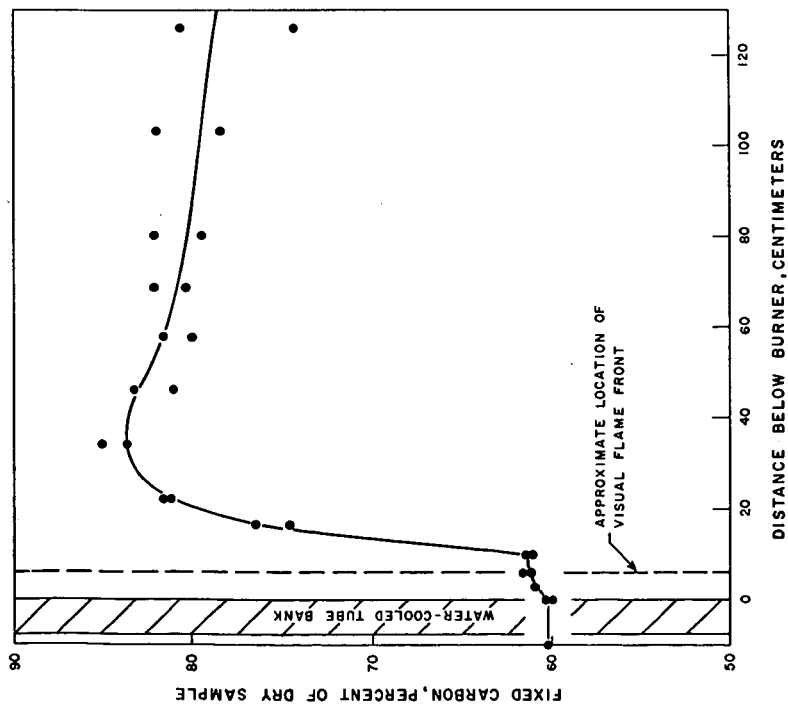
FIGURE 9
FIXED CARBON CONTENT OF SOLID MATERIAL DURING PASSAGE
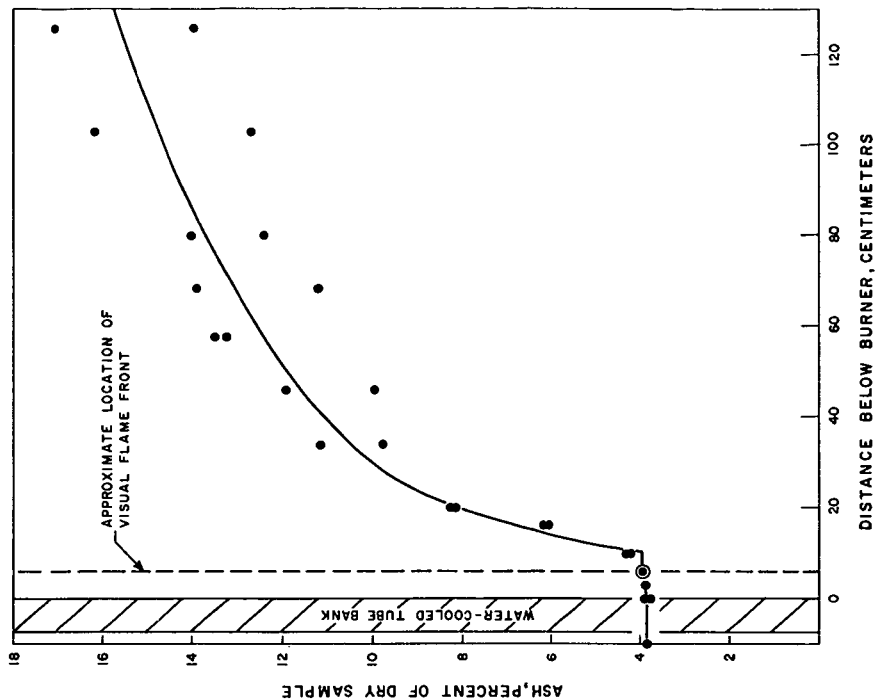THROUGH FLAME

FIGURE 10
ASH CONTENT OF SOLID MATERIAL DURING PASSAGE THROUGH FLAME

solid state along with fixed carbon. Owing to the very small decrease in volatile matter content ahead of the flame front, the rate of combustion of "solid" volatile matter immediately behind the flame front (and before the principal decomposition) would be expected to be as fast as the rate of combustion of the fixed carbon since they are burning together. Furthermore, since the temperature of the particles reaches a substantial value behind the flame front, the rate of evolution increases considerably in that region. After a period of very rapid devolatilization which 1 lasts for about 0.1 seconds, the rate of loss of volatile matter becomes so slow, although about 10 per cent of the original volatile matter still remains in the particles, that about 5 per cent of the original volatile matter is carried from the combustion chamber in the unburned solid residue.

It is instructive to observe the relative amounts of volatile matter and fixed carbon left in the solid material during the combustion process (see Figure 14). During the first 0.05 seconds in the chamber, a small amount of volatile matter is evolved while no heterogeneous combustion occurs; therefore the ratio of volatile matter to fixed carbon drops. Then, heterogeneous combustion begins at such a fast rate that the combustion of solid volatile matter is much faster than the volatile loss by gaseous evolution. Therefore, the ratio of volatile matter to fixed carbon remains essentially constant over a period of about 0.03 seconds while around 10 per cent of the original fixed carbon is burned. Meanwhile, the temperature of the particles becomes so high that the principal pyrolysis reaction, when it finally sets in, is very fast, and the loss of volatile matter by gaseous evolution is much faster than the loss by heterogeneous combustion. Therefore, the ratio of volatile matter to fixed carbon drops rather rapidly over a period of around 0.07 seconds while another 30 per cent of the original fixed carbon is burned. At this point, only about 10 per cent of the original volatile matter is left in the solid material, and the rate of evolution for this last portion is so low that the loss by heterogeneous combustion is again relatively fast and the ratio of volatile matter to fixed carbon decreases very little during the rest of the journey through the flame. This means that the loss of volatile matter in the last 80 per cent of the length of the flame is mainly by heterogeneous combustion.

8.1.2 Qualitative Models - A general, qualitative model, idealizing the progress of pyrolysis, which satisfies these data was selected by eliminating alternative models that were suggested. Of all the models initially proposed for testing, all but two were eliminated because of obvious disagreements or contradictions with the data. The difficulty of choosing between these two survivors required the more detailed analysis outlined below (see Section 8.1.4). Cenosphere formation is not included in these models since the occurrence of cenospheres under the conditions of rapid combustion found in the flame has been shown to be unlikely. (20)

(i) Model A is one in which devolatilization is assumed to occur uniformly throughout each coal particle during the whole combustion process. Heterogeneous combustion would be assumed to occur at the surface of the particle so that the particle shrinks as it moves through the flame. Since the volatile material remaining in the particle at any time is uniformly distributed, the rate of combustion of solid volatile matter is always a certain fraction of the rate of combustion of fixed carbon, this fraction being equal to the ratio of volatile matter to fixed carbon, and varying through the flame as shown in Figure 14.

(ii) Model B is one which devolatilization is assumed to occur in a thin, moving reaction zone (pyrolysis wave) which is located initially at the surface of the particle; as the particle moves through the flame, the zone moves inward toward the center of the particle. The zone leaves behind a porous matrix which contains the original fixed carbon as well as a component of the volatile matter which is relatively slow to evolve. The unreacted core situated inside the reaction zone is identical in composition to the original coal. Heterogeneous combustion occurs at the surface, and continually shrinks the size of the particle. The proportion of volatile matter being burned in the solid state depends upon the relative speeds of pyrolysis and heterogeneous combustion. If pyrolysis is faster, the pyrolysis zone moves inward so fast that the heterogeneous reaction is left behind at the surface of the porous matrix. In this case, the rate of combustion of solid volatile matter is a constant fraction of the rate of combustion of fixed carbon: the fraction is equal to the ratio of volatile matter to fixed carbon left behind by the devolatilization zone. If the rate of heterogeneous combustion is relatively fast compared to the rate of pyrolysis, the surface of the particle regresses as rapidly as the inward movement of the pyrolysis zone. In this case, both pyrolysis and heterogeneous combustion can occur simultaneously at the surface of the particle, and the loss of volatile matter by heterogeneous combustion can be taken as the total loss of volatiles.

8.1.3 Agreement of Models with Experimental Behavior

(i) Model A satisfies the data as follows: In the region of the combustion chamber between the lower surface of the water--cooled tubes and the flame front, pyrolysis occurs uniformly throughout the particle and, since the surface of the particle has not yet ignited, no fixed carbon burns; therefore, the ratio of volatile matter to fixed carbon in the particle drops. Then, the
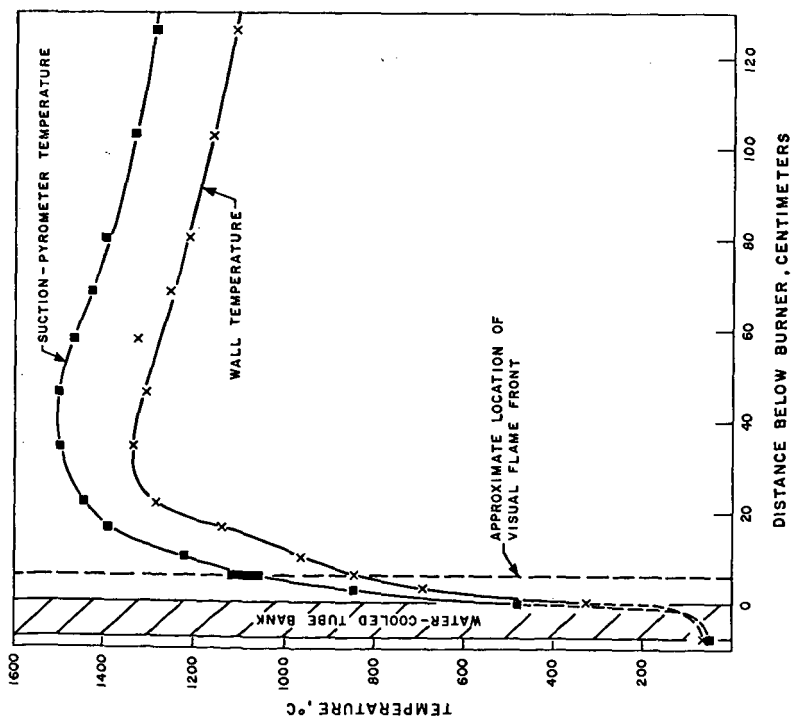
FIGURE 12
RELATIONSHIP BETWEEN VOLATILE MATTER CONTENT OF
SOLID MATERIAL, TEMPERATURE, AND TIME

FIGURE 11
SUCTION-PYROMETER TEMPERATURE OF FLAME AND
TEMPERATURE OF INSIDE SURFACE OF COMBUSTION
CHAMBER

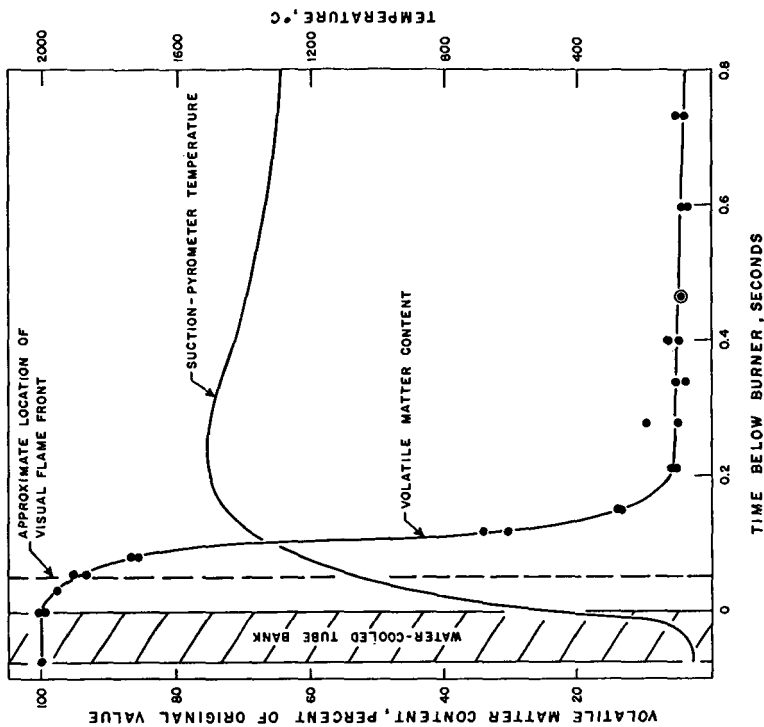solid particle begins to burn very rapidly while pyrolysis continues at a relatively slow rate; so, therefore, the ratio of volatile matter to fixed carbon remains essentially constant since both materials are burned in approximately the same proportion in which they existed at the onset of heterogeneous combustion. Next, the rate of pyrolysis increases to such an extent that the fraction of volatile matter in the burning particle drops very rapidly while the heterogeneous reaction continues relatively slowly. When only about 10 per cent of the original volatile matter remains in the particle, the rate of pyrolysis becomes so slow that the main source of volatile matter loss is heterogeneous combustion at the shrinking surface of the particle. Therefore, since volatile matter is not completely eliminated from a particle until the solid material is completely burned away, particles which are too large to burn completely in the combustion chamber carry some volatile matter with them as they leave the chamber.

(ii) Model B satisfies the data as follows: The pyrolysis zone starts moving inward as soon as the particle enters the chamber. Until the flame front is encountered, no heterogeneous combustion occurs so the ratio of volatile matter to fixed carbon drops. By the time the surface of the particle begins to burn, the pyrolysis zone is located a certain distance inward from the surface so heterogeneous combustion occurs at the surface of a porous material in which the ratio of volatile matter to fixed carbon is both very small and approximately constant. For a short time immediately following ignition, the regression rates of both the pyrolysis zone and the surface of the particle are such that the ratio of volatile matter to fixed carbon remains approximately constant for the particle as a whole; then the particle becomes so hot that the pyrolysis zone moves sufficiently fast to increase the distance back to the shrinking surface of the particle, to the ratio of volatile matter to fixed carbon decreases. When the pyrolysis zone reaches the center of the particle, the only volatile matter remaining in the solid is the component which is slow to evolve, so the main source of volatile loss in the rest of the combustion process is heterogeneous combustion. Volatile matter and fixed carbon burn together in approximately the same proportion in which they were left by the passing of the pyrolysis zone, since, except for a slow loss of volatile matter by pyrolysis, the ratio of volatile matter to fixed carbon remains approximately constant in the rest of the flame. As in the case of Model A, volatile matter is not completely eliminated from a particle until the solid material is burned away, so large particles can carry volatile matter from the combustion chamber. Qualitatively, therefore, both models are identically comparable with observation.

8.1.4 Tests of Models - According to Model A, pyrolysis occurs uniformly throughout the particle, so the rate of reaction at any time is proportional to the mass (or volume) of unreacted material (volatile matter) still present in the particle, i. e. , pyrolysis is a volumetric reaction. Since the total mass (or volume) of material is independent of the size of the particles in which it is contained, this model indicates that pyrolysis should be independent of particle size; therefore, Model A can be disproven if it can be shown that the rate of pyrolysis is dependent upon particle size.

According to Model B, pyrolysis occurs in a thin zone surrounding a solid nucleus in which the volatile matter has not yet reacted. Since the total mass of volatile matter present in such a zone is proportional to the total surface area of the particle, this model indicates that pyrolysis is a surface reaction. Surface reactions are dependent upon particle size; therefore, Model B can be disproven if it can be shown that the rate of pyrolysis is not particle-size dependent.

Model B is considered to be disproved by the following points: (1) The observed time required for pyrolysis is much larger than that predicted from Model B; (2) evidence from the literature (13) indicates there is no influence of particle size on the rate of pyrolysis for particles less than about 60 microns; and (3) calculation of the temperature distribution inside a coal particle in a flame indicates that pyrolysis could not be a surface reaction due to a temperature distribution inside the particle. Each of the above points is amplified below.

(1) Essenhigh (6) found experimentally that the time required to pyrolyze burning coal particles in the size range 0. 3 - 5 mm is proportional to the square of the original particle diameter; Essenhigh (6) then showed this result to be in agreement with the proposition that, in the case of particles in the above size range, pyrolysis can be represented by a model in which the rate of devolatilization is governed by diffusional escape of the volatiles from a shrinking reaction zone to the surface of the particle. Model B is effectively identical to Essenhigh's model with regards to the diffusional escape of volatiles, and is therefore suitable for the size range 0. 3 - 5 mm.

Assuming that the pyrolysis of particles in the pulverized fuel range (0 - 200 microns) also obeys Model B, two cases are possible: either (1) Model B is obeyed and the rate of devolatilization is controlled by the rate of pyrolysis (chemical control) or (2) Model B is obeyed and the rate of devolatilization is controlled by the rate of diffusion of volatiles to the surface of the particle (physical control). The weight fraction of the original volatile material (V/V_o) remaining in the particle at time (t) is given by the following equations (see Appendix A) :
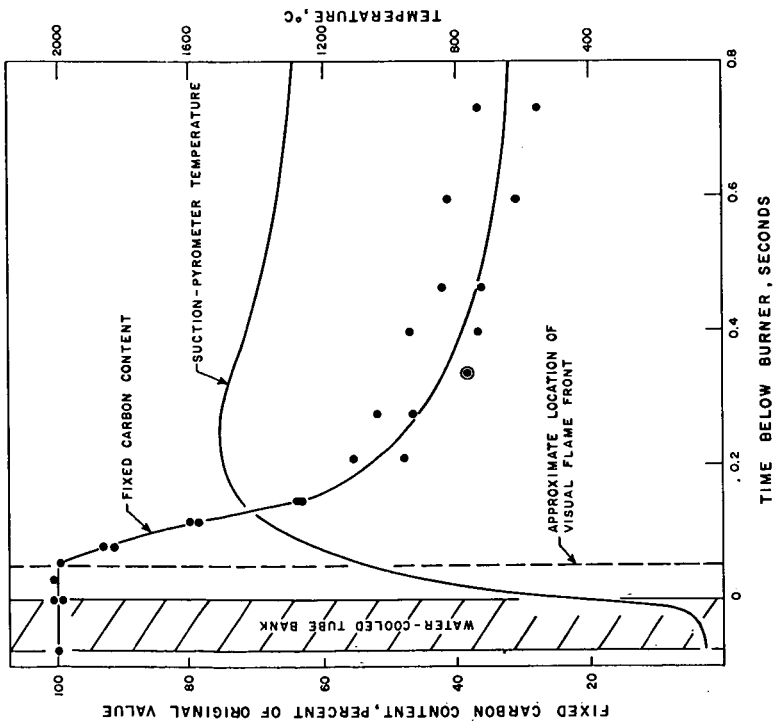
FIGURE 14
VARIATION OF COMPOSITION OF SOLID MATERIAL
WITH DEGREE OF BURN-OUT

FIGURE 13
RELATIONSHIP BETWEEN FIXED CARBON CONTENT OF
SOLID MATERIAL, TEMPERATURE, AND TIME

Case (1), chemical control: $(V/V_o) = (1 - t/t_v)^3$ (3)

Case (2), physical control: $2(V/V_o) - 3(V/V_o)^{2/3} + 1 = t/t_v$ (4)

where $t_v = K_1 d_o$ for Case (1) and $t_v = K_2 d_o^2$ for Case (2), t_v is the time required to completely devolatilize a particle of initial diameter d_o, and K_1 and K_2 are constants.

We tested Model B by employing Equations (3) and (4) along with the particle-size distribution (see Figure 7) to calculate the fraction of the original volatile material remaining in the particles at any time after ignition. This was accomplished by separating the particles into several size fractions, analyzing each fraction individually, and then combining the results to construct the total volatile decay curve. Pyrolysis was assumed to begin at the flame front, an assumption which is not far from correct (see Figure 12). Essenhigh's (6) experimental value was taken for K_2 and K_1 was estimated by assuming that chemical rate control is impending in the case of the smallest particles (0.3 mm) studied by Essenhigh (6), thus providing the boundary condition $K_1 d_o = K_2 d_o^2$ at $d_o = 0.3$ mm. The results obtained are shown in Figure 15.

The volatile decay rate predicted from Model B is far too large, with the predicted pyrolysis times being about 90-fold too small. This conclusion is the same whether physical or chemical control is accepted, and implies strongly that the dependence of pyrolysis rate on particle size, which is known to occur in the case of particles above 0.3 mm, is not obeyed by particles in the pulverized fuel size range. The extrapolation of results obtained from larger particles down to the p.f. range leads to the prediction of pyrolysis rates which are much too large because, below a certain size, further increase in pyrolysis rate with decreasing particle size is not obtained. Therefore, Model B is unacceptable for particles in the p.f. range.

(2) The above result agrees with the observations of Ishihama (13) who studied the influence of particle size on the lower-limit concentration for inflammability in dusts of several bituminous coals. His results, which are very relevant in the present argument since he studied particle sizes in the p.f. range, show that the influence of particle size upon the concentration required for a lower-limit mixture diminishes as particle size decreases, and below about 60 microns, the effect of particle size becomes inappreciable. Since pyrolysis would be expected to play approximately the same role in inflammability measurements as in a stabilized flame, this observation indicates that pyrolysis rate is independent of particle size when dealing with particles less than around 60 microns. The particle diameters of the coal used in the present investigation were mainly less than this size, so Ishihama's observation should be applicable here.

(3) Information concerning the type of reaction occurring in a coal particle was obtained by calculating the temperature distribution through the particle during the heating process. If the center of the particle is much cooler than the surface, a reasonable assumption would be that the rate of pyrolysis is faster at the surface of the particle and that pyrolysis therefore behaves like a surface reaction. Alternatively, if the temperature distribution is found to be uniform throughout the particle, pyrolysis would seem to be a volumetric reaction. Since the rate of heating is very rapid in a pulverized coal flame, conditions might be expected to be favorable for a nonuniform temperature distribution in which the surface of the particle is much hotter than the center. On the other hand, since pulverized coal sizes are very small, the rate of transport of heat to the center of the particle might be expected to be so fast that the temperature gradient remains rather flat.

The problem of calculating the temperature distribution in a coal particle moving through a flame is one in unsteady state heat transfer and required the consideration of a simplified case in order to avoid mathematical difficulties. The use of this maneuver, although losing generality, still allowed useful results to be attained, particularly of limiting conditions that overestimate the time taken to reach equilibrium.

The case considered is a spherical bituminous coal particle, initially with a uniform temperature profile, suddenly subjected to such rapid heating that the temperature of the surface rises by a certain increment while the inside of the particle remains unchanged. The surface temperature is then held constant while heat flows into the particle; the time required for the temperature of the center to rise by a certain fraction of the initial increment experienced by the surface is indicative of the magnitude of the temperature gradient existing in the particle under real conditions. If the time required for the temperature of the center of the particle to come close to that of the surface is large on the time scale of events in the flame, the temperature of the center of the particle being heated in the flame probably lags behind that of the surface by a significant amount. Alternatively, if the required time is comparatively small, the center of the particle is probably approximately as hot as the surface throughout the heating period.

General mathematical solutions presented graphically in the literature (23) were used, along with physical properties of bituminous coal, in order to obtain a quantitative solution to this
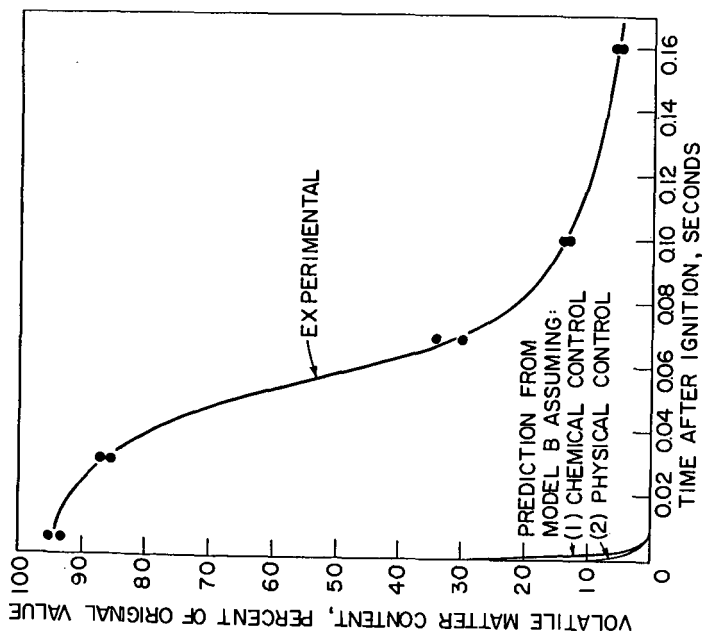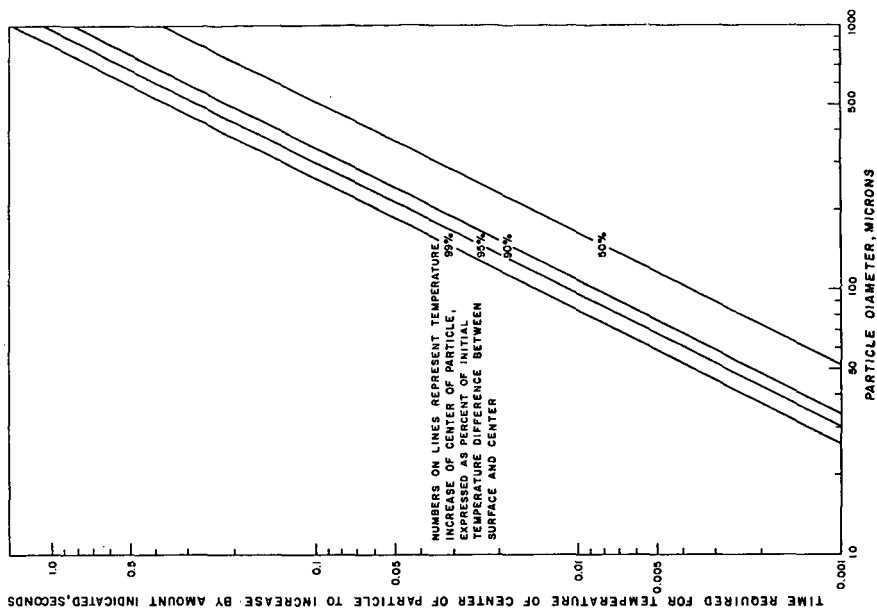
FIGURE 16

INFLUENCE OF PARTICLE SIZE UPON TIME REQUIRED FOR CENTER
OF SPHERICAL COAL PARTICLES TO HEAT BY A CERTAIN AMOUNT

FIGURE 15

COMPARISON OF EXPERIMENTAL VOLATILE DECAY RATE
WITH PREDICTION FROM SURFACE REACTION MODEL

problem. The heat absorbed (or generated) by pyrolysis was neglected on the grounds that this has been shown to be a trivial quantity. (14) The results obtained (see Figure 16) indicate that heat transport into the center of the particle is so fast that a significant temperature gradient probably could be neither created nor maintained in particles in the p. f. size range. For example, if the surface temperature of a particle initially at 100°C should suddenly reach 1100°C, about 0.02 seconds would be required for the center to reach 1090°C in the case of a 100 micron particle, and less than 0.001 seconds would be required if the particle size was 30 microns. Both these times are suitably small, especially since the probability of the occurrence of such a drastic temperature gradient is very low and the number of particles as large as 100 microns in pulverized fuel is very small. The conclusion is therefore that pyrolysis is probably not a surface reaction created by a nonuniform temperature distribution.

Data from this and other investigations, as well as the above heat transfer analysis therefore disprove Model B. The inference is that Model A, with the proposition that pyrolysis is a volumetric reaction, is therefore acceptable as there are no experimental grounds for discarding it.

QUANTITATIVE ANALYSIS

9.1 Loss of Volatile Matter

The selection of Model A allows the loss of volatile matter to be described in more detail. The goal of the detailed description is to divide the total loss of volatile matter into two parts, namely, that lost by pyrolysis and that lost by heterogeneous combustion.

At any time t, the total weight of volatile matter lost from the coal is Δ (V. M.) and can be expressed by the equation

$$\Delta (V.M.) = \Delta V_V + \Delta V_S \tag{5}$$

where ΔV_V and ΔV_S are the weights of volatile matter lost by evolution into the gaseous state, and by heterogeneous combustion, respectively.

According to Model A,

$$dV_S = \left[(V.M.)/(F.C.) \right] d(F.D.) \tag{6}$$

where V.M. and F.C. represent the weights of volatile matter and fixed carbon, respectively, and V_S is that part of V.M. which will be lost eventually by heterogeneous combustion. Integration of this equation from the lower surface of the water-cooled tube bank to any point in the combustion chamber provides the following expression for the fraction of the original volatile matter which has been lost by heterogeneous combustion when the coal reaches that point:

$$\left[(\ V_S)/(V.M.)_o \right] = - \int_1^X \left[(V.M.)/(F.C.) \right] / \left[(V.M.)/(F.C.)_o \right]$$

$$d \left[(F.C.)/(F.C.)_o \right] \tag{7}$$

where $x = (F.C.)/(F.C.)_o$, $\Delta V_S = (V_S)_o - V_S$, and the subscript o refers to the value of a quantity at the lower surface of the water-cooled tube bank. The negative sign before the integral is necessary since the quantity $d \left[(F.C.)/(F.C.)_o \right]$ is negative.

Equation 7 was integrated graphically. It represents the area under a certain portion of the curve formed by plotting $\left[(V.M.)/(F.C.) \right] / \left[(V.M.)/(F.C.) \right]$. An example of this curve has already been discussed (see Figure 14). Values for $(\Delta V_S)/(V.M.)_o$ were thus obtained.

Since the fraction of the original volatile matter which has been lost by both processes is

$$\Delta (V.M.)/(V.M.)_o = 1 - \left[(V.M.)/(V.M.)_o \right]$$

the fraction lost by pyrolysis is, according to Equation 5,

$$\Delta V_V / (V.M.)_o = 1 - \left[(V.M.)/(V.M.)_o \right] - \left[\Delta V_S/(V.M.)_o \right] \tag{8}$$

This equation was easy to evaluate since values for $\Delta V_S/(V.M.)_o$ were provided by Equation 7, and values for $(V.M.)/(V.M.)_o^S$ were provided by the data (see Figure 12).

Evaluation of Equations (7) and (8) thus provided a division of the volatile loss into two parts (see Figure 17). It is found that roughly 70 per cent of the original volatile matter is lost by gaseous evolution while about 25 per cent is lost by heterogeneous combustion.

The above analysis provides a basic picture of the process by which volatile matter is lost from the particles, and permits detailed analyses of pyrolysis which would be impossible without this knowledge of the influence of heterogeneous combustion.
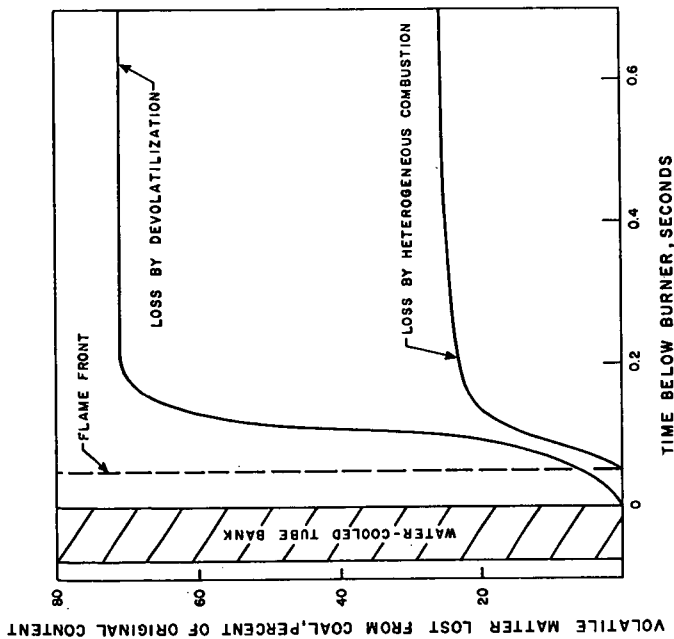
FIGURE 18
ARRHENIUS PLOT FOR EVOLUTION OF VOLATILE MATTER

FIGURE 17
LOSS OF VOLATILE MATTER BY HETEROGENEOUS COMBUSTION
AND BY DEVOLATILIZATION

9.2 Kinetics of Volatile Evolution

Pyrolysis has already been shown to be first-order with respect to the amount of volatile matter left in the solid material (see Section 8.1). The rate of the reaction is therefore given by the expression:

$$d \left[(V.M.)/(V.M.)_o \right] /dt = -k_V \left[(V.M.)/(V.M.)_o \right] \qquad (9)$$

where V.M. is the weight of the volatile matter left in the solid material at any time t, $(V.M.)_o$ is the initial value of V.M., and k_V is the pyrolysis rate constant. Assuming that pyrolysis is an activated process, we may write

$$k_V = (k_o)_V \left[\exp(-E_V/RT) \right] \qquad (10)$$

where $(k_o)_V$ is the frequency factor, E_V is the activation energy, R is the ideal gas constant and T is the absolute temperature.

An attempt to fit the data with Equations (9) and (10) revealed that pyrolysis of the particles in the flame occurs as though the volatile matter exists in the coal in two components, namely, Component I and Component II. Component I decomposes fast enough to be evolved in the flame; but Component II is much slower to decompose, most of it remaining in the solid material after Component I has been evolved. The main loss of Component II is by heterogeneous combustion in the tail of the flame. The volatile matter leaving the combustion chamber in the unburned solid material (see Figures 8 and 12) is part of Component II which, according to these data, represents about 15.5 per cent of the total volatile matter in the original coal. This means that, at the point in the flame where evolution of Component I is essentially completed, the composition of volatile matter in the solid material is about 7.9 per cent of the dry, ash-free material. The devolatilization loss shown in Figure 17 can be taken as a close approximation to the decay of Component I.

The division of the volatile matter into two components has been shown to be in general agreement with the literature.(8) Also, the observation that the slow evolution of Component II allows a significant amount of volatile matter to leave the combustion chamber in the unburned solid residue agrees with the data of Saji (18), who studied flames of pulverized bituminous coal and found that the solid material leaving the furnace contained around 7.5 per cent volatile material. Another point of interest is that the data from the present investigation indicate that the composition of the solid material when the evolution of Component I has just been completed corresponds roughly with the composition at Van Krevelen's (22) carbonization pole.

The experimental data were used to evaluate the activation energy for the evolution of Component I. The rate constant was calculated from Equation (9). The value of the quantity d $\left[(V.M.)/(V.M.)_o \right]$ / dt at any location in the flame is given by the slope of the devolatilization curve (see Figure 17) at the appropriate point. Values of the quantity $\left[(V.M.)/(V.M.)_o \right]$ were obtained from a smooth curve drawn through the data (see Figure 12). Since the data give the volatile content of both Component I and Component II, the correct values for this calculation were obtained by subtracting away the amount contributed by Component II.

After obtaining a complete profile of k_V through the flame, E_V was evaluated for Component I by plotting $\ln(k_V)$ against $(1/T)$. According to Equation (10), the slope of the line obtained is $(-E_V/R)$ and the intercept is $\ln(k_o)_V$. The activation energy thus found is different in the preignition and postignition regions of the flame (see Figure 18). The average values found for the different experimental runs are as follows:

E_V in the preignition region = 6 kcal/mole

E_V in postignition region = 28 kcal/mole

The above values imply that pyrolysis ahead of the flame front is much less temperature dependent than is postignition pyrolysis. The very small activation energy found in the preignition region of the flame indicates that the pyrolysis occurring before ignition involves only very loosely held molecules. Between the burner and the flame front, the major part of the material being evolved probably consists mainly of carbon dioxide and water molecules which were held very loosely in the pores of the original coal.

The activation energy found in the postignition region are about half as large as values which Van Krevelen (21) quotes from the carbonization of coal. This suggests that the pyrolysis reaction occurring in the pulverized-coal flame may be different from that occurring in the relatively slow carbonization process. The activation energy obtained in the postignition zone is for a process occurring in only 0.1 seconds, while Van Krevelen's values are for processes which last for about 1 hour; therefore, different reactions might be expected to occur in the two processes. One possible explanation for the difference is that Component II of the volatile matter is very slow to be evolved because of a high activation energy. In the flame, events are so rapid

that this component is relatively inert with respect to pyrolysis and therefore does not affect the experimental value of activation energy. In slower processes, however, Component II has time to react and therefore could be responsible for the relatively high observed value of the "effective" or "global" activation energy.

10. INFLUENCE OF PYROLYSIS ON IGNITION AND FLAME PROPAGATION

The above data can also be used in a further analysis designed to determine whether ignition in the pulverized coal flame occurs first on the solid surfaces of particles or in gaseous volatiles. The object of the analysis is to evaluate the role of pyrolysis in ignition and flame propagation. If ignition occurs in gaseous material, then the rate of flame propagation is governed by the rate of pyrolysis ahead of the flame front; alternatively, if ignition occurs on the surfaces of solid particles, then the flame speed is independent of the kinetics of pyrolysis. (10) Again, the method of exclusion was employed, the reasoning being that the correct description of the mechanism of ignition can be obtained by disproving its alternative.

10.1 Proposed Models
Two models were constructed for testing: (i) Model C advocates that ignition occurs first on the solid surfaces of particles, with the gaseous material being ignited later following the heterogeneous combustion; (ii) Model D supports the proposition that ignition occurs first in gaseous volatiles, and solid particles are then ignited by gaseous combustion.
Model C can be disproved if it can be shown that the ignition temperature disagrees with accepted values for the ignition temperature of solid surfaces. Model D can be disproved if it can shown that an inflammable gaseous mixture does not exist at the flame front.

10.2 Test of Models
10.2.1 Complete Mixing Assumed – Before describing the detailed testing of the above models, we should like to point out that the balance of the circumstantial evidence is unfavorable to Model D, thus implying that ignition occurs first on the solid surfaces of particles. Since only a small amount of pyrolysis occurs before ignition (see Figure 8), and since a concentration of combustible gases of only 0.02 per cent by volume was found by using gas chromatography to analyze samples collected from the preignition zone of the flame with a water-cooled gas sampling probe, the existence of a combustible gaseous mixture at the flame front appears unlikely. Assuming complete mixing, an analysis of the data at the flame front shows that the maximum volatile concentration attained before ignition is around 0.0026 grams per grams of air, a value which is short of a combustible mixture by a factor of 10 even if carbon dioxide and water are neglected and all the volatiles are assumed to be methane. If the gas analyses mentioned above are included in the analysis, again assuming well mixed conditions, the maximum concentration of combustible gases before ignition is found to be 300 fold short of an inflammable mixture. However, in spite of this evidence against Model D, the possibility can still exist that the mixing of volatiles into the ambient air is slow enough to permit the establishment of an inflammable gaseous mixture around the surface of each particle by the time the flame front is reached. This possibility is explored below.
10.2.2 Limited Mixing Considered – Although mixing is both diffusional and turbulent, the latter type can be neglected as a first approximation since there should be very little relative motion between the particles and the ambient air in the preignition zone of the flame (Reynold's Number is around 2000). Assuming particles to be spheres, the flow of volatiles away from the surface of the particle can be described by the following equation which was obtained by adapting the standard Stephan flow equation to spherical coordinates, and imposing the condition that the net rate of flow of volatiles away from the particle is equal to the rate of their production by pyrolysis:

$$(P_v)_r = 1 - \underline{/}\,1 - (P_v)_s\,\underline{/}\,\exp(a^{-1} - r^{-1})\,K \tag{11}$$

where

$$K = (RT\,\mathcal{Y}_c a^3/3DPM_v)\,\underline{/}\,(\%\ V.M.)_o/100\,\underline{/}\ \ d\underline{/}(V.M.)/(V.M.)_o\,\underline{/}\ /\ dt$$

and where: $(P_v)_r$ = partial pressure of volatiles at any distance (r) from the center of the particle; $(P_v)_s = (P_v)_r$ at the surface of the particle; R = ideal gas constant; T = absolute temperature at the location being considered; $\mathcal{Y}_c$ = density of coal; a = radius of the coal particle; D = coefficient of diffusion of volatiles into air; P = total pressure; M_v = average molecular weight of volatiles; $(\%V.M.)$ = percentage of volatile matter in the original coal; $(V.M.)/(V.M.^o)_o$ = fraction of the original volatile matter remaining in the coal at the location being considered; t = time measured from the lower surface of the water-cooled tubes.

Equation (11) indicates that the profile of the concentration of volatiles around a particle is strongly dependent upon the size of the particular particle being considered, with large particles being surrounded by a higher concentration of volatiles than that around the small ones. This condition is enhanced, but not created, by the selection of Model A since, other things being equal, the flux of volatiles leaving the surface of a particle decomposing by a volumetric reaction increases roughly in proportion to particle size. The implication of this effect is that a relatively large, spherical particle can be visualized as being composed of two concentric, spherical shells, with the common center located at the center of the particle. The inner radius of the smaller shell coincides with the surface of the particle. The common surface of the shells is located at a radial distance where the concentration of volatiles equals the upper limit value for an inflammable mixture. The outer surface of the outside shell is situated at a radial distance corresponding to a lower limit concentration. In the region defined by the smaller shell, the concentration of volatiles is assumed to be so high that no ignition can occur, while the region defined by the larger shell contains an inflammable mixture. Beyond the large shell, the concentration is too low to be ignited.

When this description is applied to extremely small particles, Equation (11) shows that the radii of the hypothetical spheres are equal to (or theoretically less than) the particle radius. This means that no inflammable mixture exists around such particles.

In the case of medium sizes, the outer surface of the larger shell is still maintained away from the particle even though the smaller shell has disappeared. The meaning of this situation is that the material adjacent to the surface of the particle is inflammable, but the location of the lower limit boundary is only a small distance from the surface.

This creates for us the following picture: There exists a critical particle size below which the concentration of surrounding volatiles is too low to support ignition, while, above the critical size, an inflammable mixture is present around the particle, though it is not necessarily adjacent to the surface. The experimental data were used in conjunction with Equation (11) to make a quantitative estimation of the critical size in order to provide evidence for the trial of Model D.

The evaluation of Equation (11) was hampered to a certain extent by insufficient knowledge about boundary conditions. However, by assuming that $(P_v)_r = 0$ when $r \gg a$, the particle radius was found to be

$$a = (K')^{-1/2} \left\{ \ln / 1 - (P_v)_s / ^{-1} \right\}^{1/2} \tag{12}$$

where
$$K' = (RT \, \rho_c / \, 3DPM_v) \, / \, (\%V.M.)_o/100 / \left\{ d \, / \, (V.M.)/(V.M.)_o / \, / \, dt \right\}$$

The critical radius $(a_c)_1$ can be found by imposing the condition $a = (a_c)_1$ when $(P_v)_s = (P_v)_{L.L.}$, where $(P_v)_{L.L.}$ is the partial pressure of volatiles in a lower limit mixture with air. If the volatiles being evolved at the flame front are assumed to be composed chiefly of methane, an assumption grossly in favor of Model D, $(P_v)_{L.L.} = 0.05$. Therefore, when these conditions are substituted into Equation (12), the critical

$$(a_c)_1 = \sqrt{ / (0.153)DPM_v/RT_i \, \rho_c / \, / -\frac{(\%V.M.)_o}{100} / \left\{ d \, / \, (V.M.)/(V.M.)_o / /dt \right\}_i \, dt_i } \tag{13}$$

where the subscript (i) denotes the point of ignition.

The experimental data were used to evaluate Equation (13). The term $d / (V.M.)/ (V.M.)_o /$ / dt is the slope of the devolatilization curve (see Figure 17) at the point of ignition; T_i is the ignition temperature (see Figures 12 and 13); and since the volatiles are assumed to be methane, M_v is 16 g/mole and D is $0.157 \, (T_i/273)^{1.75} \, cm^2/sec.$ (17) if T_i is expressed in Kelvin degrees. The average of the values of $(a_c)_1$ calculated for the different experimental runs is 130 microns. Owing to our neglect of (a) turbulent mixing and (b) the presence of carbon dioxide and water in the volatiles liberated in the preignition zone, this calculated value, though serving as a lower limit, is probably too low by a factor of 2 or 3. Since only a very small fraction of the particles in pulverized fuel is as large as 130 microns, the critical diameter can be regarded as above the pulverized fuel range, thus ruling out the existence of particles surrounded by combustible gaseous mixture.

10.3 Accepted Model (Conclusion)

The conclusion from the above analysis is that the rate of transport of volatiles away from the surface of the particles in the preignition zone of the flame is fast enough to prevent the accumulation of an inflammable gaseous mixture around the particle surfaces. Hence, ignition at the flame front cannot occur in gaseous material, and Model D must be excluded. The strong inference is, therefore, that ignition originates on the solid surfaces of particles; hence Model C

is accepted by exclusion of Model D. Furthermore, the adoption of Model C receives support from the agreement between the ignition temperature observed in this investigation (around 1100°C, see Figures 12 and 13) and values reported in the literature for comparable conditions. (15, 19) The rate of flame propagation can, therefore, be regarded as independent of the rate of pyrolysis.

11. SUMMARY

The pyrolysis of particles in pulverized coal flames was studied by probing a one-dimensional flame. The object of the investigation was to fill a gap which existed in the knowledge of pulverized fuel combustion, and at the same time to improve the understanding of coal pyrolysis. The flame studied was produced in a system employing a new type of "burner", and the water-cooled probes used were developed and tested in this investigation. Measurements were made of the flame temperature and the composition of the solid material in the preignition and postignition regions of the flame as well as in the flame front.

The data thus collected were employed in an analysis designed to formulate a picture of pyrolysis and to evaluate the effect of pyrolysis on flame propagation. The following conclusions were drawn:

(1) The particles attain a temperature of about 1100°C before either ignition or a significant amount of pyrolysis occurs. The rate of pyrolysis does not become significant until after ignition. After a period in which the rate is very rapid, pyrolysis then becomes so slow that about five per cent of the original volatile material leaves the combustion chamber in any unburned solid residue.

(2) Pyrolysis and heterogeneous combustion occur simultaneously, thus making impossible a division of the flame into two distinct zones, one containing only devolatilization and the other containing only solid combustion.

(3) Volatile matter is lost from the particles by both heterogeneous combustion and gaseous evolution; the latter mode of loss accounts for slightly less than 3/4 of the total loss.

(4) Pyrolysis occurs as though the volatile matter in coal is composed of two different components, one of which is evolved very rapidly while the other is much slower to be evolved. The slow-evolving component seems to represent about 15 per cent of the total volatile matter.

(5) Pyrolysis of particles in the pulverized-fuel size range (0-200 microns) is evidently a volumetric reaction occurring uniformly throughout each particle; the rate of pyrolysis in the flame is therefore independent of particle size.

(6) The activation energy of pyrolysis was found to be about 6 kcal/mole in the preignition zone and about 28 kcal/mole in the postignition zone of the flame.

(7) Ignition was found to occur on the surfaces of solid particles instead of in gaseous volatiles; hence the rate of flame propagation is independent of the rate of pyrolysis.

ACKNOWLEDGMENTS

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APPENDIX

According to Model B (see Section 8.1), a pyrolyzing spherical coal particle of initial radius r_0 can be visualized as a spherical core (radius = r) of unreacted material surrounded by a spherical shell of thickness $(r_0 - r)$. Pyrolysis occurs at the surface of the unreacted core, producing volatile material which diffuses through the surrounding porous matrix to the surface of the particle. The following analysis produces two equations describing the relationship between the weight fraction V/V_0 of the original volatile material left in the particle at time t : one equation describes the case in which the rate of devolatilization is controlled by the rate of diffusion of volatiles out of the particles (physical control), and the other one describes the alternate case in which the rate of pyrolysis is the limiting step (chemical control).

Case I (Physical Control) - According to Essenhigh (6), the equation describing the above model under conditions of physical control should be of the form

$$(r - r^2/r_0) \, dr = - (r_0^2/6t_v) dt \qquad (A1)$$

where t_v is the time required for complete devolatilization. Integration of Equation (A1) between the limits $r = r_0$ at time $t = 0$ and $r = r$ at $t = t$, together with the substitution $(r/r_0)^3 = (V/V_0)$, produces the following result.

$$2(V/V_0) - 3(V/V_0)^{2/3} + 1 = t/t_v \qquad (A2)$$

Case II (Chemical Control) - In this case, at a given temperature, the rate of devolatilization is proportional to the surface area of the unreacted core, and is expressed as follows:

$$d(V/V_0)/dt = K(r/r_0)^2 \qquad (A3)$$

where K is a constant. Since $(V/V_0) = (r/r_0)^3$, Equation (A3) can be integrated between the limits $(V/V_0) = 1$ at $t = 0$ and $(V/V_0) = (V/V_0)$ at $t = t$. When a value is obtained for K by imposing the condition $(V/V_0) = 0$ at $t = t_v$, the resulting expression is found to be:

$$(V/V_0) = (1 - t/t_v)^3 \qquad (A5)$$